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Supercritically-Dried Alginate Aerogels Retain the Fibrillar Structure of the Hydrogels

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Summary: SAXS patterns of a Ca-alginate hydrogel and of the derived alcogel and aerogel have been recorded. All patterns correspond to disordered arrays of rod-like fibrils. The calculated size of the fibrils of the aerogel, 8 nm, is in good agreement with the results of scanning electron microscopy and N_2 adsorption. The results suggest that ethanol exchange and CO_2 supercritical drying do not affect the spatial organisation of the secondary structures of the gel and that characterisations of the aerogel can provide information on the organisation of the parent hydrogel.

Keywords: aerogels; alginate; polysaccharides; SAXS; secondary structure; textural properties

Introduction

Alginic acids are natural block copolymers produced by brown algae, with (1–4)-linked β-D-mannuronic (M) and α-L-guluronic (G) residues.[1] The structure of the two uronic acid monomers (pyranose rings bearing a carboxylic group) are represented in Figure 1.

Like other polyelectrolytes, alginic acids form mechanically stable hydrogels which are effective storage media for water solutions. This property is at the basis of their natural occurrences in algae of the tidal area[3] as well as of their uses as thickeners in the food industry,[4,5] encapsulation and drug release media in the pharmaceutical[6–8] and phytosanitary industry,[9] and vectors for enzymes and yeasts in biological detergents[10] and industrial fermentation.[11]

Alginic acid-based gels can be formed according to two different mechanisms: physical (pH-driven) and ionotropic gelation. In the formation of alginic acid hydrogels, the pH of a Na-alginate solution is lowered, the Na^+ cations are exchanged by protons and the hydrogen bonds between carboxylic groups form bridges between the polymer chains. Ionotropic alginate hydrogels are formed by exchanging a Na-alginate solution with multivalent cations. Divalent cations which compensate the charge of two carboxylate groups form bridges between the polymer chains. The different orientation of the (1–4)-links of the uronic residues, axial in the case of guluronic and equatorial in the case of mannuronic, accounts for variations of the organization and stability of the gels formed by alginates with different ratios and sequences of the monomers.[12,13] The conformation of the guluronate sequences is especially suited for the coordination of divalent cations by several oxygens of the polymer, according to the so-called egg-box model, which can account for the mechanical stability of alginate and pectin gels.[14–16]

If the chains of alginate can be isolated in solution or form transient junction zones

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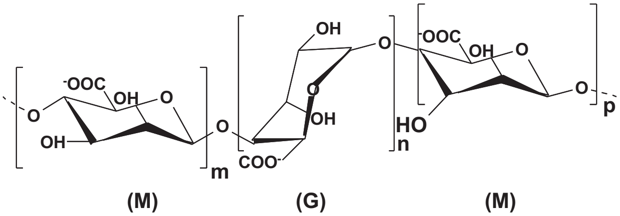

Figure 1.
Structural units of alginic acid: (M) mannuronic and (G) guluronic residues.[2]

between double helices at the beginning of gelation,[17] they aggregate and form secondary structures when enough divalent cations are available.[18] The early steps of gelation have been monitored by SAXS for both physical[19–22] and ionotropic gelation.[23–26] The observation of supercritically-dried gels has shown that stable gels are formed by an open network of fibrillar secondary structures.[27–29] The high dispersion of the fibrils in the hydrogel is at the basis of the application of alginates as ion exchangers for water remediation[30] or as heterogeneous catalysts for reactions in aqueous solution.[31]

Supercritically-dried alginate aerogels have been shown to retain most of the volume of the parent hydrogel and to present surface areas as high as 700 m^2 g^{-1}.[32,33] The accessibility of the acid sites of alginic acid aerogels has been evidenced by adsorption of basic probe molecules.[2] Alginate aerogels have been tested as supports for metal catalysts[34] and as adsorbents of polar molecules from hydrocarbon solutions.[35]

The purpose of this communication is to ascertain if the high surface area of the aerogels and the retention of the hydrogel volume in the aerogel correspond to a conservation of the fine structure of the hydrogel through the different steps of its transformation in aerogel.

Preparation and Characterization of the Aerogel

Hydrogel beads were prepared by adding drops of a 1% (w/w) solution of Na-alginate (Sigma-Aldrich from Macrocystis pyrifera, 35% guluronate groups) to a stirred 0.24 molar $CaCl_2$ solution. The beads were ripened in the solution for 18 h before being extracted from the solution and washed with distilled water.

Liquid CO_2 and water are not directly miscible. As a consequence, in order to prepare the beads for supercritical drying, the hydrogel beads had to be dehydrated by immersion in hydroalcoholic solutions of increasing ethanol concentration (10, 30, 50, 70, 90 and 100%).[36] In this way, alcogel beads were formed. Ethanol was later exchanged by liquid CO_2 in a Polaron 3100 apparatus, in which the samples were heated beyond the CO_2 critical point (31 °C, 74 bar) and outgassed to obtain the aerogel beads. The aerogel beads retained most of the volume of the parent hydrogel beads.[32]

A scanning electron micrograph of the cross-section of an aerogel bead was recorded on a Hitachi S-4500 apparatus and is reported in Figure 2. The aerogel is

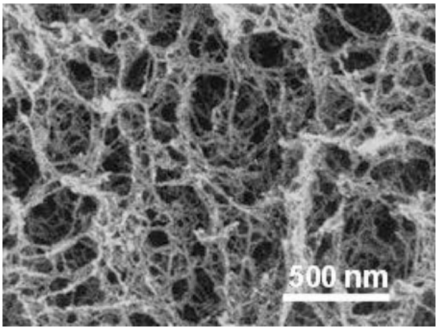

Figure 2.
Scanning electron micrograph of a cross-section of Ca-alginate aerogel.

formed by an open network of fibrils 200–300 nm long with 5–8 nm diameter.

Volumetry of N_2 adsorption at $-196\,°C$ was performed in a Micromeritics ASAP 2010 apparatus on a sample outgassed at $50\,°C$. The surface area S of the aerogel, as calculated by the BET method by assuming a molecular area of 0.162 nm^2 for the adsorbed N_2, was 385 $m^2\ g^{-1}$. It has been shown that crystalline guluronate presents the same cell parameters of crystalline guluronic acid.[37] Under the assumption that the aerogel fibrils present the same molar volume as crystallized alginic acid,[38,39] the fibrils should present a volumic mass $\rho = 1.79\ g\ cm^{-3}$. Under the further assumption of a cylindrical shape of the fibrils, their average diameter can be calculated as $D = 4 / (S\ \rho) = 5.7$ nm.

SAXS Experiments and Their Significance

In order to define at which extent the texture of the aerogel is an image of the texture of the parent hydrogel, samples representative of the different stages of the hydrogel-aerogel conversion have been characterized by SAXS. The SAXS data were collected at an incident photon energy of 16 KeV at the BM2-D2AM beamline at the European Synchrotron Radiation Facility in Grenoble. The alginate beads were placed in the central hole (10 mm diameter) of a metallic sample holder (thickness 2 mm). The data were corrected for dark image, flat field response, and tapper dispersion. The radial average of the scattering data was normalized by the transmitted intensity.

The SAXS patterns of Ca-alginate hydrogel, alcogel, aerogel, and the aerogel wetted with ethanol are reported in Figure 3.

At q values lower than 0.03 $Å^{-1}$, all patterns exhibit a common asymptotic behavior close to $I(q) \sim q^{-1}$, indicative of randomly-oriented rod-like scattering objects (Figure 3).[40] In the low-q region, the patterns only differ by their intensity, which increases in the order hydrogel < alcogel < aerogel. In this region, the alcohol-filled aerogel pattern is superposed with the alcogel pattern. The variation of intensity (by a factor 20) only depends on the contrast of electron density between the polymer and its surroundings: water, alcohol or air. The SAXS patterns indicate that the rod-like character of the secondary structures of the gel is unaffected by alcohol exchange, CO_2 supercritical treatment and further wetting by a low-surface tension liquid.

The Kratky plots of the SAXS patterns are reported in Figure 4. The position of the maximum of the Kratki plot q_{max} is related to the gyration radius R° as $q_{max} = 1/R°$.[41] The diameter D of cylindrical rods can be

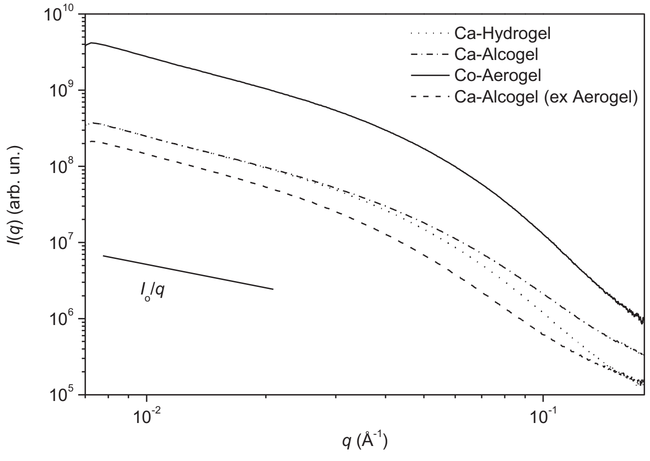

Figure 3.
Scattering patterns of Ca-alginate hydrogel, alcogel, aerogel and ethanol-filled aerogel.

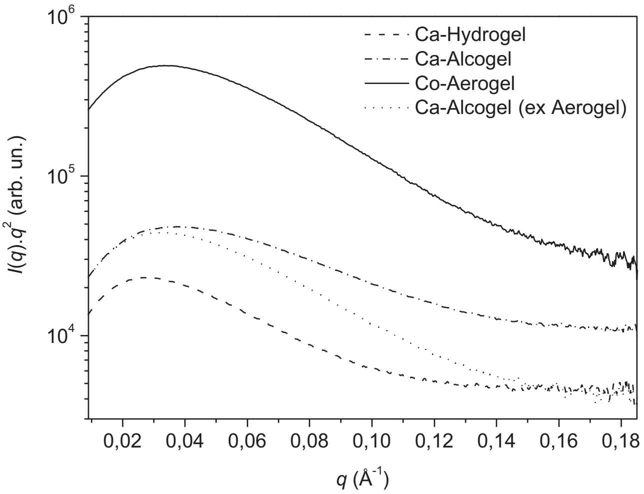

Figure 4.
Kratky plots of Ca-alginate hydrogel, alcogel, aerogel and ethanol-filled aerogel.

calculated as $D = 2^{3/2}\ R°$. The calculated diameters for hydrogel, alcogel, aerogel, and alcohol-wetted aerogel are, respectively, 9.8, 7.4, 8, and 8 nm.

It is interesting to correlate the variations of the fibril diameter with the linear shrinkage of the gel as measured by macroscopic techniques.[32] In the dehydration of the hydrogel to alcogel, the macroscopic shrinkage of the gel is very limited (1.4% linear shrinkage) while the gyration radius decreases by 28%. The more likely interpretation of this effect is that the change of solvent has brought to an increase of the density of the fibril, probably corresponding to the extraction by alcohol of some water occluded between the chains of polymer. During the CO_2 supercritical treatment, a 7.5% linear shrinkage of the gel is accompanied by a 15% increase of the gyration radius. Both effects could correspond to a change of the organisation of the polymer chains, possibly related to crystallization in dehydrated form. The geometrical stability of the aerogel when wetted by ethanol would be coherent with the formation of a stable organisation of the chains inside the aerogel fibrils.

If the internal structure of the fibrils can be affected by the changes of solvent and by drying, the retention of a rod-like morphology and the limited geometrical variations observed indicate that the texture of the polysaccharide aerogel is inherited from the secondary structures of the parent hydrogel. This suggests that physical characterizations of the supercritically-dried solid can provide information on the organisation of the parent gel. The extension of this conclusion to other gelling polysaccharide is under study,[33] as preliminary data suggest, for instance, a retention of morphology in the case of chitosan[42,43] but not in the case of κ-carrageenan.[44]

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